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EFFECT OF ION BOMBARDMENT ON THIN FILM PROPERTIES

by

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EFFECT OF ION BOMBARDMENT ON THIN FILM PROPERTIES

/1088*

Gu PeiFu and Tang JinFa[1]

Abstract

Oxygen ions from cold cathode ion guns have been used for bombarding when growing thin films. The effect of ion bombardment on film packing density and moisture absorption is examined. It was shown that the packing density of ZrO_2, TiO_2 and SiO_2 that were bombarded by ions increased to over 0.9 based on the measurement given by a quartz crystal microbalance. As a result of exposure to the moisture in a wet atmosphere, the drift of peak transmission wavelength of interference filters that are made of these materials was reduced by 2/3. This suggests that ion assisted technology maybe capable of producing thin films with superior optical and mechanical properties.

I. Introduction

Viewing from an electron microscope, most films have a column structure with a diameter of several dozens of micrometers (1, 2). The formation of this structure is a direct result of molecule deposition on the surface of the substrate or due to limited migrations of some atoms. By increasing the migrations of these adhesion atoms or molecules, the packing density of these films can be increased. A proposal was made to use low energy ion to bombard the films to increase the migration rate by supplying additional activation energy. Martin and Macleod et al (3) were able to reduce moisture induced drift of peak

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* Numbers in margins indicate foreign pagination. Commas in numbers indicate decimals.

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transmission of interference filters from 8 nm to 0.6 nm by bombarding it with 600 eV Ar ion at a flow density of 16 $\mu A/cm^2$. Hirsch and Varga (4) reduced the internal interactions by bombarding it with 1650 eV Ar ion. Herrmann and MacNeil used 50 $\mu A/cm^2$, 700 eV Ar ion to bombard MgF_2 film which is growing on a cold substrate. The durability obtained is equivalent to the one that is usually made by depositing on a 250°C hot substrate. Ebert (6) developed Heitman oxygen ion reaction technology and made 27 layer TiO_2/SiO_2 reflective mirrors. The absorption loss is smaller than $1x10^{-4}$, scattering loss is about $2x10^{-4}$. We bombarded some common oxide with oxygen ions and measured the impact on the packing density and the drift change of central wavelength in filters. We also measured scattering and refractive index. It showed that oxygen ions are very effective in improving the packing density of films.

II. EXPERIMENT DESIGN

Fig.1 depicts the set-up used in the experiment. 1 is ion gun source, 2 is ion gun, 3 is evaporation source, 4 is sample, 5 is quartz crystal detector, 6 is crystal oscillator, 7 is E312 frequency meter, 8 is D.C constant voltage source. The ion gun is used to emit oxygen ion. It is mounted on the bottom board of a film spraying machine at 20° from the vertical line of the board. The structure is shown on fig. 2. The ion gun used a cold and unfilled cathode 4, and an anode whose cap is connected to ground to prevent potential burning of the cathode. The ion output board below the anode cap is usually made of quartz glass or K_9 glass. If electron conducting metal was used instead, 60% of electrons and ions were captured in our experiment. If negative high voltage was imposed on the cathode, negative oxygen ions and electrons can be ejected from the ion gun point.

When vacuum degree reaches $5x10^{-5}$ Torr, needle valve starts to fill ion gun with oxygen. When oxygen pressure is about several Torr, a pressure gap starts to form at the little opening of ion ejecting board. The release of

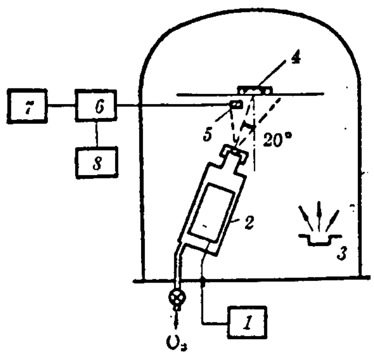

Fig. 1 Block diagram of the experimental setup

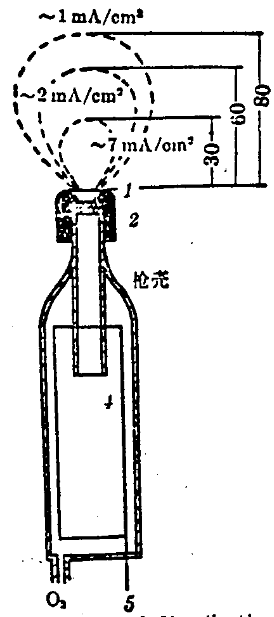

Fig. 2 Ion-gun and distribution of the current density

electric current of ion gun depends on the oxygen pressure of the tube. In order to obtain high ionic current instead of electric current, the oxygen pressure needs to be maintained at a higher level (6). The current density is measured with 1 cm^2 adhesive board at the base by adjusting the oxygen pressure and the distance between the opening and the base. The electric current density depicted on fig.2 is used to measure the ion gun. It is shown in our experiment that the current density distribution is inversely proportional to the square of the distance. The opening of the ion gun is about 80 mm from the base, the current density on the substrate is about 1 mA/cm^2 or higher using 900 V D.C. The quartz crystal is about 60 mm from the opening, the current density is 2 mA/cm^2.

Quartz crystal microbalance is used to measure and calculate the various frequencies required for packing density. Suppose F_0 is the oscillating frequency prior to the deposition, f_1 is the frequency after deposition, f_1 is the frequency after introduction of moisture vapor in vacuum chamber. The frequency change as a result of deposited film and adhesive moisture is $\Delta f_1 = f_1 - f_0,\ \Delta f'_1 = f'_1 - f_1$. If the density of column section is ρ_3, the packing density can be expressed as (8),

$$p = \frac{\Delta f_1}{\Delta f_1 + \rho_s \cdot \Delta f'_1}, \qquad (1)$$

Hence, by measuring the frequency change prior to and after evaporation and moisture absorption, the packing density can be determined

In order to reduce the frequency measurement error, the crystal must be replaced after it is coated with a layer of film. This also needs to be corrected by measuring the moisture induced frequency change in the crystal. The condensing effect by the pores of thin film correlates to the relative humidity. Introduction of moisture into vacuum chamber will saturate the relative humidity which will lead to the filling of the pores with water. Only then can the real packing density can be measured.

The refractive index of the thin film is measured with a UV-240 spectrophotometer, the accuracy in transmission is better than 0.3%. The following formulas are used to calculate refractive index (9)

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$$T_m = \left[1 - \left(\frac{1-n_s}{1+n_s}\right)^2\right]\frac{T_F}{T_0}, \qquad (2)$$

$$n_F = \left\{n_s\left[\frac{2}{T_m} - 1 + \sqrt{\left(\frac{2}{T_m} - 1\right)^2 - 1}\right]\right\}^{\frac{1}{2}}, \qquad (3)$$

In which T_F is the maximum transmission when the thickness is odd numbers of $\lambda/4$. T_0 is the transmission of the substrate at this wavelength. n_s is the refractive index at the basement.

The evenness of film layer refractive index is designed as q, $q = n_G/n_A$, the ratio of the refractive indexes of films at the side of glass and in the air. When wavelength is number 2, the refractive index of the uneven film can be expressed as:

$$R_I = \left(\frac{n_s n_A - n_G}{n_s n_A + n_G}\right)^2, \qquad (4)$$

Hence,

$$q = n_s \frac{1-\sqrt{R_I}}{1+\sqrt{R_I}}, \qquad (5)$$

If q=1, it is an even film; if q<1, it is a positively changing uneven film. Inversely, it is a negatively changing uneven film.

The single layer film is deposited at room temperature, the temperature of multilayer film is about 100° C. The vacuum degree is $2\text{-}3 \times 10^{-4}$ Torr in ion bombarding and depositing, otherwise it is 5×10^{-5} Torr.

III. Results

1. Single layer film

The data on commonly used oxide such as ZrO_2, TiO_2 and SiO_2 is listed on Table 1. As it is shown in the table, ion bombarding the growing film during the deposition can greatly improve the packing density. The increase in measured film refractive index is also an indication of an increase in packing density. In addition, the unevenness of ZrO_2 film refractive index shows ion bombardment causes the positive changing in the refractive index, i.e. $n_A > n_G$. This also indicates a higher packing density. Ion bombarding also cause an increase in diffraction in most cases.

2. Multilayer Film

Since ion bombardment causes an increase in packing density in a single layer film, naturally a similar effect would be expected to be found in multilayer film. Three different materials, ZrO_2, TiO_2 and SiO_2 are used to make light filters to observe the drift in wave. The data is listed on table 2.

The drift of filters can be reduced by 2/3 after ion bombardment. Fig.3 is the measured transmission curve. Fig.3(a) is the curve prior to moisture absorption (curve 1) and after moisture absorption (curve 2) of $(HL)^4$ H4LH$(LH)^4$ ZrO_2-SiO_2; Fig.3b is the curve prior to moisture absorption (curve 1) and after moisture absorption (curve 2) of $(HL)^2$ H4LH$(LH)^2TiO^2$-SiO_2. It showed that maximum transmission and half thickness of the film hardly changes during the drift. However, the curve shifted toward the long wave. The transmission of an ion bombarded filter also has been improved considerably due to the use of high refractive index materials.

Sample 3 uses TiO as starting material, it has higher absorption due to the omission of ion bombardment. Two filters were dried together in air at 300°C for two hours. As a result, the total drift is greatly reduced. /1091

Table 1 Experiment results of single layers

1 材料	2 序号	3 有无轰击	几何厚度 (Å) 4	聚集密度 p 5	散射 (%) 6		折射率 $n_F(\lambda)$ 9	非均匀性 q 12
					7 膜层	8 衬底		
ZrO_2	1	有 10	600	0.94	0.15	0.11	1.79(860)	0.986
		无 11	990	0.61	0.14		1.73(860)	1.048
	2	有 10	700	0.92	0.11	0.07	1.84(660)	0.988
		无 11	690	0.64	0.08		1.75(670)	1.012
TiO_2	1	有 10	1800	0.90	0.19	0.17	2.09(670)	
		无 11	2100	0.69	0.20		1.36(690)	
	2	有 10	660	0.92	0.11	0.03		
		无 11	2360	0.72	0.07			
SiO_2	1	有 10	2980	0.93				
		无 11	3710	0.86				
	2	有 10	1670	0.92	0.13	0.06	1.45(680)	
		无 11	1990	0.83	0.12		1.44(720)	

Key: 1. material, 2. sequence number, 3. bombardment, 4. thickness, 5. packing density, 6. scattering, 7. film layer, 8. film bottom, 9. refractive index, 10. yes, 11. no, 12. unevenness.

Table 2 Peak wavelengths drift for interference filter with and without bombardment

序 1 号	膜 系 2 结 构	轰击否 3	漂移前的中心 4 波长 (nm)	大气中的漂移量 (nm) 5	100%相对湿度中的漂移(nm) 6
1	$G(HL)^4H4LH(LH)^4A$ $H—ZrO_2$, $L—SiO_2$	有 7	550	3.5	7.0
		无 8	540	15.3	20.2
2	$G(HL)^3H4LH(LH)^3A$ $H—ZrO_2$, $L—SiO_2$	有 7	510	6.6	8.8
		无 8	530	17.7	20.0
3	$G(HL)^2H4LH(LH)^2A$ H—TiO 作初始材料 $L—SiO_2$	有 7	545	2.7	3.4
		无 8	540	6.9	8.7
4	$G(HL)^2H4LH(LH)^2A$ $H—TiO_2$, $L—SiO_2$	有 7	550	2.8	7.0
		无 8	580	10.7	膜裂

Key: 1. sequence number, 2. film structure, 3. bombardment, 4. central wavelength prior to drift, 5. drift in the air, 6. drift in 10% relative humidity, 7. yes, 8. no.

The moisture absorption by filters occurs primarily at the initial air contacting stage. Two hours after completion of filters, N_2 gas is used to fill the filters. The wavelength drift can exceed more than half of the total within the first half hour exposure to air.

A computer was used to simulate data on packing density of single layer film and drift in filters. In table 1, the packing density after ion bombardment is $P_{ZrO_2}=0.94$, $P_{TiO_2}=0.92$ and $P_{SiO_2}=0.92$. The packing density without bombardment is 0.65, 0.7 and 0.85. The filter composed of ZrO_2-SiO_2 $(HL)^4$ $H4LH(LH)^4$ has a drift of 9 nm and 25 nm with or without of bombardment. The corresponding drift for TiO_2-SiO_2 filter $(HL)^2$ $H4LH(LH)^2$ is 9 nm and 22 nm. These results fit well with the data in Table 2.

It is also shown that the stability of bombarded film was improved dramatically. It is equivalent to the stability of the film that is obtained at higher substrate temperature (200°C).

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IV. DISCUSSION

It is very effective to improve the film packing density by increasing the deposition molecule or atom migration rate with the ion assisted bombardment. Quartz crystal is used to measure the packing density of a single layer film. The packing density can be increased by increasing the temperature on the base board. The packing density of film at higher base board can be measured by indirectly measuring the wavelength drift of film in vacuum chamber after moisture absorption. In addition, by increasing the energy and dosage of bombarding ions, a greater impact can be achieved, but this is invariably accompanied by an increase in scattering loss. This means that current method in achieving higher packing density and still maintaining the low scattering loss left a lot to be desired.

Oxygen ion assisted bombardment can increase oxidation and decrease the absorption caused by dissociation. Materials with lower combination capability tend to dissociate strongly if heated and vaporized, such as In_2O_3 and SnO_2. When these films were bombarded by oxygen ions, absorption can be reduced substantially. The accurate measurement of absorption due to oxygen ion bombardment requires condition that is beyond our capability. But oxygen bombardment is not beneficial to fluoride, sulfuride and semiconductor film. Instead inert gas such as Ar should be used. Therefore, the ion gun needs reconstruction to meet this need.

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